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Photodegradation of Aromatic Polyimides

by

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The photolysis results for a soluble polyimide, 6F-ODA, based on 2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane dianhydride (6F) and 4,4'-oxydianiline (ODA) were compared to the polyimides, PMDA-ODA and BTDA-ODA, based on, pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), which were reacted with ODA. All the photolyses involved the exposure of thin polymeric films to a medium pressure mercury lamp (unfiltered) in air. The IR, UV, and weight loss results for the polymers suggest that an ablative process occurs upon photolysis. The spectral and weight loss changes were much greater for 6F-ODA. Dilute solution viscometric and gel permeation chromatographic analyses of the pristine and photolyzed 6F-ODA points toward a very rapid and efficient chain scission process along the polymer backbone. The strength of the charge transfer (CT) interactions in the respective polymers may explain in part the greater UV stability observed for the PMDA-ODA and BTDA-ODA. (KR)

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PHOTODEGRADATION OF AROMATIC POLYIMIDES

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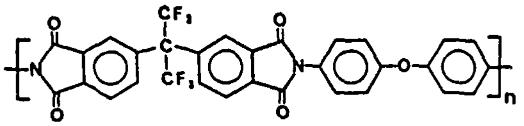
Introduction

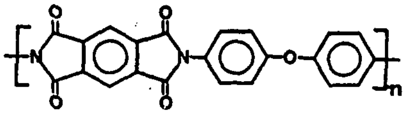
Aromatic polyimides continue to be of major commercial importance as a result of their thermal and oxidative stability, chemical resistance, and outstanding mechanical properties among others. In many applications such as coatings, exposure to UV radiation may be encountered. Few reports, however, are available on the photostability of aromatic polyimides [1-5].

The initial polymeric system chosen for our study on the photodegradation of aromatic polyimides were based on a perfluorinated dianhydride (6F) and 4,4'-oxydianiline (ODA).



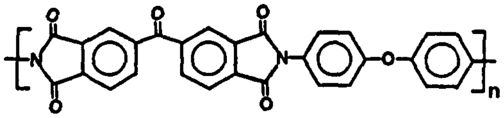
6F-ODA

Polyimides made from this monomer are soluble in common organic solvents without sacrificing any of the characteristic properties of polyimides listed previously. Since insolubility is often a problem in the processing of polyimides, great interest has been shown in such soluble polymers. Solubility also affords the use of a greater number of characterization tools such as gel permeation chromatography (GPC) and viscometry in which to investigate the photodecomposition process. The results for the 6F-ODA polymers are compared to a pyromellitic dianhydride (PMDA)-based polyimide



PMDA-ODA

and a 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)-based polyimide.



BTDA-ODA

Experimental

Materials

Polymer grade 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride (6F, Hoechst Celanese) was used without further purification for the lower molecular weight polyamic acid synthesis. The 6F was vacuum sublimed prior to use for the higher molecular weight polyamic acid synthesis. Pyromellitic dianhydride (PMDA, Aldrich) was recrystallized from methyl ethyl ketone and vacuum sublimed prior to use. The 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA, Aldrich) was washed with dry methyl ethyl ketone and vacuum sublimed before using. 4,4'-Oxydianiline (ODA, American Tokyo Kasei) was recrystallized from ethanol and sublimed under vacuum. Dimethylacetamide (DMAc, Aldrich) used as the solvent in the polymerizations and the viscometric analyses was dried over molecular sieves and fractionally distilled under vacuum from calcium hydride. Tetrahydrofuran (THF, J.T. Baker) used in the GPC was distilled under nitrogen from calcium hydride.

Synthesis

The synthesis of the initial polyimides involved the dissolution of the diamine in DMAc in a nitrogen-purged flask and the addition of an equimolar amount of dianhydride dissolved in DMAc. The reaction mixture contained 15 weight % solids and was stirred at room temperature for eight hours. The inherent viscosities of the polyamic acids synthesized for 0.5 weight % solutions in DMAc at 35 °C were as follows: 6F-ODA, 0.69 dL/g; PMDA-ODA, 1.19 dL/g; BTDA-ODA, 1.27 dL/g. The polyamic acid solutions were poured onto soda lime glass plates and spread using a drawbar that produced a 4 mil thick wet film. The polyamic acids were thermally converted to polyimides by heating in a Blue M forced air oven. The temperature program used in the curing process involved 20 minutes at 60 °C, 1 hour at 100 °C, 1 hour at 200 °C, and 1.5 hours at 260 °C. There was a ramp time between isothermal settings. The glass plates were placed in hot water to facilitate the removal of the polyimide films.

The polyimides which were cured at different maximum temperatures were synthesized by simultaneously dissolving the two monomers in DMAc and using sublimed 6F in the case of 6F-ODA in an effort to produce higher molecular weight polyamic acids. Inherent viscosities of the polyamic acids synthesized for 0.5 weight % solutions in DMAc at 35 °C were as follows: 6F-ODA, 1.26 dL/g; PMDA-ODA, 1.91 dL/g. The as cast films were placed in a vacuum oven at room temperature for 30 minutes to produce tacky films. Thermal curing was carried out in a Blue M Inert Gas Oven. Purging took place for 30 minutes at an elevated nitrogen flow rate to remove the air from the sample chamber. The temperature program involved 1 hour at 100 °C, 1 hour at 200 °C, and 1 hour at a maximum cure temperature. The maximum cure temperatures used were either 250, 300, 350, 400, or 450 °C. Heating and cooling occurred at 5 °C per minute and 2 °C per minute, respectively. A continuous nitrogen purge was maintained throughout the thermal curing process.

Characterization

Infrared absorption spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer with a 4 cm^{-1} resolution. A Perkin-Elmer Lambda 6 UV-VIS spectrophotometer with 1 nm resolution was used to record the UV absorption spectra. The fluorescence emission spectra were obtained from a SPEX Fluorolog-2 spectrofluorometer using 1.5 mm slit widths for the excitation and emission monochromators. The fluorescence emission from the films was measured in the front face geometry. The GPC analyses were carried out using the following conditions and equipment: solvent, THF; flow rate, 1.0 mL/min.; 100, 500, 10^4, and 10^5 A Waters Ultrastyragel columns; Waters 410 differential refractometer. The calibration curve was based upon a series of polystyrene standards (Polysciences). Molecular weights were determined from the peak maxima of the elution curves. Inherent viscosity measurements were obtained using an Ostwald size 100 bore viscometer. 0.2 weight % solutions were prepared and equilibrated at 35 °C.

Photolysis

The film photolyses were conducted using the unfiltered output of a 450 W Canrad Hanovia medium pressure mercury lamp in air. The films were place approximately 9 cm from the lamp.

Results and Discussion

Figures 1-2 show the IR and UV spectra of 6F-ODA before and after exposure for 20 hours to the full arc of a medium pressure mercury lamp in air. Upon photolysis a uniform decrease in absorbance is observed over the entire IR spectrum without the appearance of any new bands. The UV absorbance spectrum of the photolyzed material is blue-shifted compared to the pristine polymer. Similar IR and UV spectral analysis of BTDA-ODA and PMDA-ODA films show such polymers to experience only slight changes upon photolysis for equivalent times. The IR and UV results for the 6F-ODA polyimide films suggest that an ablative process is occurring under the photolysis conditions employed. This explanation is borne out by the results from weight loss studies depicted in Figure 3. After 20 hours of exposure to an unfiltered medium pressure mercury lamp in air, the 6F-ODA experienced a weight loss of 36% whereas the BTDA-ODA and PMDA-ODA lose only 12% and 9%, respectively.

Solution characterization of 6F-ODA reveals a very rapid decrease in molecular weight accompanying the weight loss during photolysis. This decrease in molecular weight is illustrated in the change in inherent viscosity with photolysis time seen in Figure 4. The same behavior is observed in the GPC analysis of the unphotolyzed and photolyzed materials displayed in Figures 5-6. These results point toward a very rapid and efficient chain scission process along the backbone during the photodecomposition of 6F-ODA. Both photodegraded and pristine materials were completely soluble in THF indicating the absence of any crosslinking.

A possible explanation for the great difference in photostability between the 6F-ODA, BTDA-ODA, and PMDA-ODA is the degree of interchain interaction in the form of charge transfer (CT) complexes present in the respective polymers. Dine-Hart and Wright [6] first proposed the presence of CT interactions in aromatic polyimides to account for their color, solubility, thermal stability, and mechanical properties. Kotov [7] and Ishida [8] provided spectroscopic evidence for this proposition. Fryd [9] has used the CT argument to rationalize a number of properties characteristic of polyimides. The strength of these CT complexes is dependant on the electron affinity of the dianhydride moiety and the ionization potential of the diamine moiety. Introduction of separator linkages, sterically bulky groups, and meta-orientation into the polyimide backbone can effectively disrupt chain packing and thus reduce these intermolecular interactions [2].

In the film state at room temperature approximately 300° C below the glass transition temperature (T_g), the additional flexibility introduced by the 6F group is not expected to induce photolability. In the case of 6F-ODA, one might expect that the electron-withdrawing ability of the perfluoro groups would serve to increase the electron affinity of the dianhydride and lead to a stronger CT complex. The steric bulk of these groups, however, may prevent close enough approach or proper orientation of the chains to one another to form a strong CT complex. In contrast, PMDA is the prototypical dianhydride since it does not contain any of the structures that serve to decrease the degree of CT interaction. BTDA also forms stronger CT complexes than 6F. For PMDA-based polyimides the experimentally-determined interchain distance [10] is less than the theoretical interchain distance for phenyl group rotation [11] which is a reflection of these interactions.

A final note concerning the presence of a CT state in the 6F polyimide is in order. Using fluorescence spectroscopy Frank [12] reported that an emission above 500 nm from PMDA-ODA occurs from an excited CT complex. At high cure temperatures he believes this rather strong emission is due to enhanced intramolecular coplanarization and intermolecular aggregation. Both phenomena are reported to contribute to an increase in the stabilization of CT complex formation. The fluorescence emission spectra for 6F-ODA films cured at different temperatures are shown in Figure 7. Apparently the 6F-ODA cured at 300 °C and 350 °C display the same type of emission spectra as that reported for PMDA-ODA polyimides cured at similar temperatures. However the PMDA-ODA emission, although not shown here, is distinctly red-shifted compared to the emission for 6F-ODA in Figure 7. This may well indicate that the 6F-ODA CT complex is not stabilized in the excited state to the same extent as the PMDA-ODA CT complex. This explanation is consistent with our supposition that a more stable CT complex for PMDA-ODA accounts for the increased stability toward photodegradation.

Our results show the dramatic effect of chemical structure on the photolytic degradation of high temperature resistant polyimides. The differences in the photostability of the various polyimides may be explained at least in part by their ability to form stable charge transfer complexes. In particular, polyimides based on the 6F perfluorinated dianhydride form weaker CT complexes than the BTDA and PMDA polymers and degrade quite rapidly upon exposure to the complete spectral output of a medium pressure mercury lamp in air. Our preliminary work suggests that the interplay between chemical composition and spectral/electronic properties in polyimides is critical in obtaining UV-resistant films.

Acknowledgement

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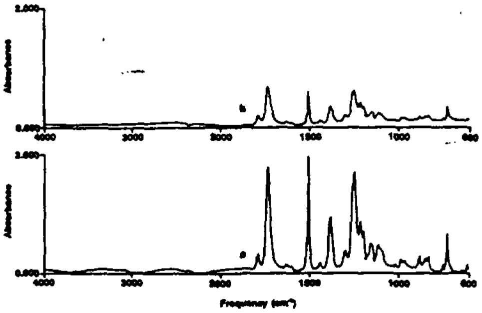

Figure 1. IR spectral change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered). (a) 0 h; (b) 20 h.

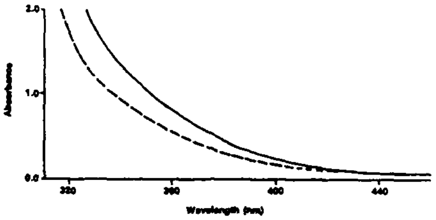

Figure 2. UV spectral change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered). (a) 0 h, (——); (b) 20 h, (– – –).

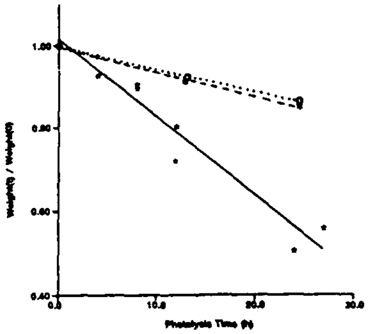

Figure 3. Weight change for photolysis of polyimide films in air using a medium pressure mercury lamp (unfiltered). (a) 6F-ODA, (★,——);
(b) BTDA-ODA, (✱,– – –); PMDA-ODA, (✪,•••••).

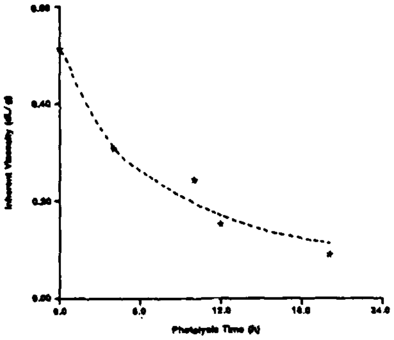

Figure 4. Inherent viscosity change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered).

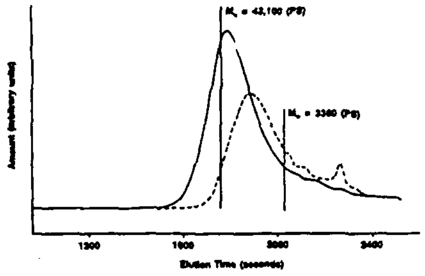

Figure 5. GPC curve change on photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered). (a) 0 h, (——); (b) 20 h, (– – –).

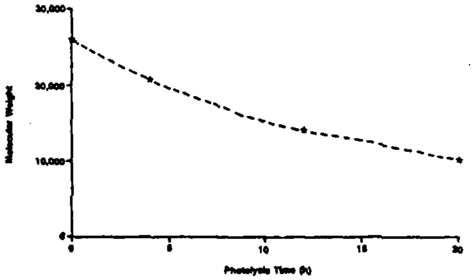

Figure 6. Change in molecular weight at peak maxiumum (M_{max}) upon photolysis of 6F-ODA films in air using a medium pressure mercury lamp (unfiltered).

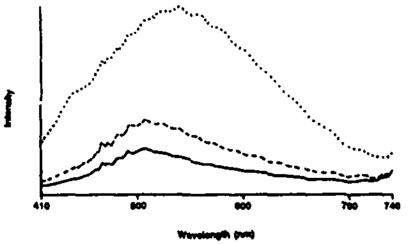

Figure 7. Fluorescence emission spectra (λ_{ex} = 380 nm) for 6F-ODA cured at different maximum cure temperatures. (a) 250 °C, (——); (b) 300 °C, (– – –); 350 °C, (•••••).